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(54) Title: DRILLING FLUIDS AND METHODS OF USING THEM (57) Abstract The oil component of an oil based drilling fluid that is used for carrying out of a subsea bore hole debris that may then be dumped in the sea while still contaminated with the oil is a mineral oil that is substantially non-toxic to marine life and that is of low viscosity at 40°C and at lower temperatures.		

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DRILLING FLUIDS AND METHODS OF USING THEM

Drilling fluids are used to carry debris, such as drill cuttings, out of a bore hole during the drilling of the hole or during other operations within the hole. Thus the fluids are circulated down the hole and carry the debris up the hole. Throughout this specification we use the term "drilling fluids" in the generic sense to mean the fluids (sometimes called muds) that are intended to be used during the actual drilling of an oil well or other bore hole as well as the fluids that are intended to be used at other stages, for instance the work over or completion of a well, such other fluids sometimes being known as work over fluids or packer fluids.

The debris that is carried from the bore hole by the drilling fluids is separated from the fluid at the head of the hole and the fluid is recycled. The debris may be dumped.

The drilling fluids consist of a liquid phase and often contain also a solid phase dispersed in it, for instance a weighting agent such as barytes. The liquid phase may consist of water in which various minor additions may be dissolved or dispersed, e.g. various gelling agents and dispersing agents. However it is often found that best results are obtained, especially during drilling, when the liquid phase includes oil, the fluids then being referred to as oil based drilling



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muds or fluids. Thus the liquid phase may consist of oil or it may be a mixture of oil and water, for instance an oil-in-water emulsion or a water-in-oil emulsion.

Numerous oils have been proposed for use as the oil in the liquid phase of drilling muds. There have been some proposals to use vegetable or other edible oils but mineral oils have generally been considered as more satisfactory and cost effective. Various mineral oils have been proposed. A typical disclosure is in British Patent Specification No. 1,467,841 in which it is stated that the oil may be diesel oil, crude oil, kerosene or other aliphatic hydrocarbons or mixtures. Another appears in US Patent Specification No. 2,969,321 in which the proposed oils are topped crude oils, gas oils, kerosene, diesel fuels, heavy alkylates and fractions of heavy alkylates. Despite all these numerous proposals the oil was generally chosen having regard primarily to availability and cost effectiveness and as a result the oil that is used in practice is generally diesel oil.

Despite the actual use of diesel oil in practice there are some examples in the literature of particular oils other than diesel oils. For instance various asphaltic, paraffinic and naphthenic oils are exemplified in US Patent Specification No. 2,698,833 and in US Patent Specification No. 3,840,460 there is an example of an oil base that is a blend of sulphurised lard oil, chlorinated paraffin and a naphthenic mineral oil. The oils exemplified in US Patent 2,698,833 generally appear unsatisfactory by today's safety standards because of their generally low flash points and the oil exemplified in US Patent 3,840,460 suffers from the cost and other disadvantages incurred in the use of oils other than mineral oils.

When the drill cuttings or other debris are



separated from the drilling fluid, e.g. at the well head, the resultant separated debris will still be contaminated with the fluid phase of the drilling mud, and therefore with the oil if it is an oil based drilling mud. When
5 the drilling is at sea the further treatment of the contaminated debris can create a problem. If the contaminating oil is toxic to marine life and the contaminated debris is simply dumped into the sea then this dumping contaminates the sea unacceptably. Diesel
10 oil has been shown to be toxic to marine life and so debris contaminated with diesel oil has to be washed before dumping but this requires extra apparatus on the rig or drilling platform and results in the generation of washings contaminated with oil, which in turn then have
15 to be separated or treated further before they can be discharged.

In U.S. Patent No. 3,594,317 the problems arising from the anti-pollution regulations concerning the use of oils in drilling muds are discussed and it
20 is stated that it has become necessary to find materials other than oil which will provide the attributes of oil in drilling mud. The proposal in that specification is to use decyl alcohol as a component of an aqueous based mud. Whilst this may avoid pollution problems decanol
25 is not a satisfactory and cost effective alternative to oil in drilling muds, especially in the more difficult bore holes where sticking of, for instance, the drill pipe is a particular risk.

Recent tests in USA have indicated that the
30 mineral seal oil available in USA from US refineries under the trade name Mentor 28 can be used in place of diesel oil as the oil in an oil based drilling fluid and that the resultant fluid is less toxic to marine life than fluids based on diesel oil.

35 Also we have discovered that certain other oils, especially naphthenic oils having low aromatic



contents, have acceptably low toxicity, and indeed are much less toxic than Mentor 28 as supplied in USA.

The viscosity characteristics required of conventional muds are well known and the viscosity of the oil of the oil base in an oil based drilling mud is very significant in determining the viscosity of the mud. Diesel oils have been regarded as having particularly convenient viscosity properties, and this is one reason why they have been used so extensively.

10 We have now surprisingly appreciated that when using an oil based mud for drilling beneath the sea bed the oil of the oil base should be less viscous than diesel oil, measured at 20°C, and preferably also less viscous than diesel oil measured at 5°C. Accordingly it is now
15 appreciated that for satisfactory subsea drilling the oil of an oil based drilling mud must be both less toxic and less viscous than diesel oil, and generally also less toxic and less viscous than US Mentor 28.

A method according to the invention is one in which an oil based drilling fluid is used to carry debris out of the subsea bore hole and the debris is dumped in the sea while contaminated with the fluid and in this method the oil of the oil base must have a viscosity at 40°C of less than 6 cSt and must have acceptably low toxicity :
25 as defined below and is a mineral oil.

The oil of the oil base should at 5°C, and generally also at 20°C, have a viscosity less than the viscosity of diesel oil. This is particularly important because of the low ambient temperatures encountered in many offshore drilling operations and the difficulties that follow from funnel and plastic mud viscosities that may be too high at ambient temperatures unless oils of very low viscosity are used. Generally the viscosity at 5°C is below 15, preferably below 10, for instance 1 to 7 cSt.

35 The viscosity at 20°C should be low, generally below 15 and preferably below 10, most preferably below



8. It is normally at least 1, typically from 3 to 8 and often 4 to 7 cSt. The oil of the oil base generally has a viscosity at 40°C of below 6 cSt and preferably below 5.5 cSt. The viscosity is often in the range 1 to 5.5, 5 for instance 3 to 5. However there are indications that best results are obtained with very low values, preferably 1.2 to 3.8 cSt.

The oil preferably has a viscosity at 100°C of from 0.6 - 2.5, generally 0.7 to 1.4 cSt. All 10 viscosity measurements herein are the kinematic viscosity values obtained by ASTM 445/1P71.

Toxicity can be observed by determining the effect of a selected amount of the oil in sea water on brown shrimps (*Crangon crangon*). Healthy shrimps are 15 maintained in aerated sea water at 15°C in the presence of a selected concentration of the oil and the mortality of the shrimps after varying periods is observed. On this test diesel oil gives high mortality, e.g. above 50% and often 90 to 100% at a concentration of 100 µl/l 20 after 24 hours. The oils used in the invention give substantially no mortality (for instance below 10% and preferably below 1%) at 24 hours when present in amounts of 100 µl/l and preferably also substantially no mortality when used in amounts of 333 µl/l for 24 hours. Preferab- 25 ly the mortality at 96 hours at 100 µl/l is also low, generally being below 30% and preferably below 15% and preferably also the mortality at 333 µl/l at 96 hours is in the same range, most preferably below 15%. Generally the toxicity is such that at least 50% of the brown 30 shrimps survive for at least 5 days at oil concentrations of at least 333 µl/l and often of at least 1000 µl/l. A typical diesel oil, No. 2 diesel oil, results in only 50% survival after as little as 5.6 hours at a concentration of 100 µl/l.



We believe that some low molecular weight aromatic compounds are non-toxic and that the toxicity probably arises from the presence of some or all of the polynuclear aromatic compounds, where poly represents at least 4 benzene rings and generally 5 or more, (especially benzopyrene and 1,2,5,6 dibenzanthracene) and some lower molecular weight compounds such as toluene, xylenes, phenanthrenes and possibly also naphthalenes.

The oil is preferably substantially free of, for instance, benzopyrene and other aromatic compounds that cause toxicity. By this we mean that the oil is either totally free of benzopyrene and other toxic compounds or contains them in such small amounts that the toxicity of the oil is not raised unacceptably.

Because of the uncertainty of the nature of some of the aromatic compounds in oils containing a significant aromatic content it is preferred that the oil has an aromatic content of less than 5%, preferably less than 4% and most preferably 3.5% or less. The aromatic content of an oil may be recorded by test methods such as CSL 606-4, ASTM D2007 or ASTM D2140-66. Typically it may be determined as the percentage by volume of the oil that is provided by aromatic compounds. It can be measured by calculating the proportion of carbon atoms in the oil that are present in aromatic compounds, based on the total proportion of carbon atoms in the hydrocarbon content of the oil.

With many oils there is a significant increase in toxicity between the preferred oils used in the invention, typically having aromatic contents of 0.2 to 3.5%, preferably below 2.5%, and oils containing higher contents, for instance 7 to 12% aromatics. For instance Mentor 28 in USA seems to have an aromatic content above 10% and is found to be more toxic than is desirable. However if the oil is free of toxic aromatic compounds then the total



aromatic content can be higher than 5% and may be as high as 10 or even 12%.

Preferred oils for use in the invention are naphthenic or paraffinic oils having low aromatic content.

5 Naphthenic oils may be derived from naphthenic crude and it seems that they can be much less toxic to marine life than diesel oil and US Mentor 28. The naphthenic oil may be obtained by blending two or more oils of which at least one generally is derived from naphthenic crude. For instance, a blend may be formed of an
10 oil derived from naphthenic crude and a paraffin oil, provided that the final blended oil can still be classified as a naphthenic oil. Naturally when blends are formed the blending oil must not be such as to introduce toxic
15 components, and this is discussed in more detail below.

Suitable naphthenic crude for use as the source of some or all of the naphthenic oil is Venezuelan crude. The oil may have been hydrogenated during its production from naphthenic or other crude to convert aromatic compounds to naphthenes.
20

Naphthenic oils are a well recognised class of oils clearly distinguished from paraffinic oils. They are characterised by the fact that they contain less than about 70% paraffinic (aliphatic) compounds and a substantial amount of naphthenic (cycloaliphatic) compounds.
25 For instance at least 25% and preferably at least 35 or 40% of the oil is provided by naphthenic compounds. Best results appear to be provided when the oil contains 30 to 60%, preferably 45 to 60%, naphthenic compounds, but higher amounts (for instance up to 70% or 80%) or
30 lower amounts (for instance 25 to 30 up to 45%) are sometimes suitable. The paraffinic content is preferably not more than 65%, or 70% at the most. Naphthenic and paraffinic contents can be determined as above.

35 The naphthenic oil preferably has a characterisation factor of less than 12.0 and preferably from 11.8 to 11.0 or even down to 10.0.



Naphthenic oil derived from suitable naphthenic crude can have a satisfactorily low aromatic content but if the oil is obtained by blending then the oils blended into the naphthenic oil must not be such as to introduce toxic components and so the oil that is blended with the naphthenic should also be substantially free of toxic aromatic compounds.

Low odour kerosenes and other paraffinic oils having a low aromatic content are often suitable.

10 The mineral oil (or blend of mineral oils) is preferably substantially colourless and substantially odourless. It must of course comply with safety regulations and in practice this means that it must have a flash point of at least 60°C, preferably 66°C or 15 more.

The initial boiling point of the distillation range of the oil used as the oil base is preferably below 250°C. The A.P.I. gravity value of the oil is generally at least 15 and is normally below 35.

20 Two naphthenic oils suitable for use in the invention are POLY-X-HP35 supplied by Burmah-Castrol Company and Clairsol 350 supplied by Carless Solvents of Hackney Wick, London. Typically analysis of these oils are as follows.



9

POLY-X-HP35

	Colour, Saybolt	+ 20
	Density at 20°C	0.860
	Kinematic Viscosity at 20°C cSt	6
5	Kinematic Viscosity at 40°C cSt	3.6
	Viscosity at 100°C cSt	1.1
	Flash Point (PMCC) °C	115
	Pour Point. °C	- 66
	Sulphur Content %	2.2
10	Aniline Point	91±1°C
	Aromatic Content Atoms	6%
	Naphthenic Carbon Atoms	54%
	Paraffinic Carbon Atoms	40%

15		<u>Clairsol 350</u>	
		<u>Typical Properties</u>	<u>Test Method</u>
	Odour	Good	-
	Colour	Water White	-
	Density at 15°C	0.788	ASTM D1298
20	Distillation Range °C		ASTM D 86
	Initial Boiling Point	200	
	50% Distills at	221	
	Dry Point	248	
	Flash Point °C	74	ASTM D 93
25	Kauri Butanol Value	28	ASTM D1133
	Aromatic Content v/v	0.2%	CSL 606-4
	Low Explosive Limit (% volume in air)	0.6	-
	Upper Explosive Limit (% volume in air)	7.1	-
30	Autoignition Temperature °C	230	-
	Naphthenic content	40% v/v	
	Isoparaffin content	20% v/v	
	n-paraffin content	40% v/v	
35	Threshold Limit Value (TLV) ppm	200	by calculation
	Viscosity at 20°C	2.3. cSt.	



10

Other oils having similar analysis may be used especially other naphthenic solvents, for instance having characteristics similar to Clairsol 350.

- Any of these oils can be used individually or blends can be formed of two or more of these oils or of one or more of these oils with another oil, for instance a paraffinic oil. A suitable blend is formed of 40 to 90, preferably 60 to 80, parts by volume of a naphthenic oil with a paraffinic oil, provided the blend still has a sufficiently high naphthenic content to be classed as a naphthenic oil.

- A suitable oil for use in the invention is formulated by blending 70 parts by volume of 60 Solvent Pale Oil and 30 parts by volume of Clairsol 350. Suitable 60 Solvent Pale is supplied by J.O. Buchanan of Renfrew, Scotland. The resultant blended naphthenic oil has the following properties.

Typical Properties

	Aniline Point	75.4°C
	Flash Point	96°C
	Pour Point below	-50°C
20	Viscosity at 40°C	4.19 cSt
	Distillation range -	
	Initial boiling point	214°C
	10% boiling	236°C
25	50% boiling	292°C
	90% boiling	320°C
	Final boiling point	335°C
	Estimated aromatic content	2.37%
	Specific gravity	0.849

- Another suitable oil that may be used is the product sold by Norol of Norway under their Trade Name Lameparafin.

- The oil base of the drilling fluid may consist of the described mineral oil or it may be a blend of the described mineral oil and water. At least 1% by volume of this blend must be the mineral oil and generally the amount of oil is at least 30% by volume



based on water plus oil, with the amount preferably being from 51 to 99%, most preferably 60 to 95% by volume oil, with the balance to 100% by volume being water. Depending upon the emulsifiers present and
5 the amounts of oil and water the fluid may be a water-in-oil emulsion or an oil-in-water emulsion.

The water used for forming the fluid may be fresh water or sea water and may contain dissolved salts such as sodium chloride or calcium chloride, up to
10 saturation concentrations. Thus the fluid may be an oil-in-water emulsion in which the water is a sodium chloride brine. An advantage of the use of the defined oils is that emulsions formed from them tend to be more stable than the corresponding emulsions formed from
15 other, relatively non-toxic, mineral oils such as various paraffinic oils.

The drilling fluids may contain other additives as is conventional in oil based drilling fluids and these additives may be dissolved or dispersed
20 in the oil base. Thus they may contain one or more emulsifiers, for instance, polymerised organic acids such as the product sold by the Applicant under the Trade Name Carbo-tec L and oil soluble amide polymers that are wetting agents



and supplementary emulsifiers, such as the product sold by the Applicant under the Trade Name Carbo-Mul. The amount of any emulsifiers is generally from 0.1 to 10% (of the commercial emulsifier) by volume, most preferably 5 1 to 5% by volume, based on the total volume of oil and water, or 1 to 20%, preferably 2 to 5% based on the water.

The mud may contain high molecular weight organic polymers and inorganic bridging agents, such as the mixtures sold by the Applicants under the Trade Name 10 Carbo-Trol. Lime hydrate may be dissolved in the water.

The drilling fluids will, in particular, generally contain a large amount of weighting material, such as barite, iron oxide, siderite or calcite. The amount of weighting aid is generally from 100 to 400 15 grams per 100 cc drilling fluids, for instance 200 to 500 pounds per barrel.

It is standard practice to adjust the rheological properties of oil based and other drilling fluids by including gelling agents in them. A variety of materials 20 have been proposed as gelling agents. The most widely used gelling agents are bentonites, for instance the material commercially available as DMB (drilling mud bentonite) and the products available as Sedapol 155 or Sedapol 44, or Claytone 34 or Claytone 40. They 25 can be used in the invention but better results are obtained by use of an organophilic hectorite. This may be naturally occurring hectorite or synthetic hectorite, for instance as described in British Patent Specification No. 1054111. If it is a synthetic hectorite it preferably 30 erably includes exchangeable organic ammonium cations as described in British Patent Specification No. 1121501.

The preferred materials may be described as tetraalkylammonium hectorites, as described in British Patent Specification No. 1121501. One to three of the 35 alkyl groups are preferably short chain alkyl groups (e.g. C_{1-8} most preferably C_{1-3} , typically methyl) and one to three of the alkyl groups are preferably long



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chain alkyl groups (e.g. C₁₀₋₂₅, typically C₁₄₋₂₂, most preferably C₁₈).

A preferred material is dimethyldioctadecyl ammonium hectorite, preferably Bentone 38 or Imvitone 1 or Imvitone 2, which are derivatives of naturally occurring hectorite.

The amount of gelling aid is typically from 1 to 10, most preferably 1.25 to 4, grams gelling aid per 100 cc fluid. An alternative way of expressing the amount is as 3 to 15, most preferably 5 to 9, pounds gelling aid per barrel drilling fluid. In general the amount of gelling aid required in the fluids of the invention is greater than the amount required in conventional drilling fluids, for instance being from 1.5 to 2.5 times the amount required when the oil is diesel oil.

The following are examples of the invention.

Example 1

A drilling fluid is prepared by blending 235 cc Clairsol 350, 5 cc primary emulsifier, 5 cc secondary emulsifier, 9 grams gelling aid, 42 cc calcium chloride brine, 5 grams lime, 15 grams bridging aid and 309 grams barytes. This drilling fluid is a 13 pound per gallon mud having an 85:15 oil:water ratio and an internal phase activity of 0.75. Its initial properties at 49°C are plastic viscosity 22 cps, yield point 5.5 g/100 cm² and gel strength 3/6.5 g/100cm² and after hot rolling at 65°C were plastic viscosity 23 cps, yield point 7g/100 cm² and gel strength 5/6.5g/100cm².

It is particularly suitable for use in subsea drilling where the sea temperature may be 5°C or lower.

When the oil is tested for toxicity by the method described above, it is found that after 24 hours it causes no fatality at 333 µl/l and about 4% fatality after 96 hours at 100u/l. In the same tests number 2 Diesel oil gives 93% fatality after 24 hours at 100ul/l.



Example 2

A drilling fluid is prepared from 149 cc Pale Oil 60, 63 cc Clairsol 350, 7 cc blown tall oil emulsifier, 5 cc oil soluble amide polymer as secondary emulsifier, 53 cc water containing 25% calcium chloride, 6 g lime hydrate, 7 g a blend of high molecular weight organic polymers and inorganic bridging agents, 358 g barite and 6 g dimethyldioctadecyl ammonium hectorite. Very satisfactory downhole and toxicity properties are obtained when used in a subsea bore hole followed by filtration of the debris from the fluid and dumping of the debris in sea.

Example 3

A drilling fluid is prepared as in Example 1 except that POLY-XHB35 is used in place of the Clairsol 350. The resultant fluid has low toxicity and particularly good properties under high downhole temperature conditions.

20 Example 4

A drilling fluid is prepared as in Example 2 using a Bentonite gelling aid in place of the hectorite. The resultant fluid is less satisfactory when it is allowed to cool to, say, 5°C but still gives useful downhole temperatures.



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It should be noted that best results are obtained when the oil has an aromatic content of below 15, and preferably below 5 and most preferably below 1% by volume when measured by ASTM 2007 (especially when the oil is a naphthenic solvent) or, if it is an insulating oil, when its aromatic content is below 5% when measured by ASTM 2041. When measured by infra red the aromatic content may be below 10, preferably below 6, for instance 0.1 to 5% (compared to about 12% for US Mentor 28 and 18-20% for Diesel).



CLAIMS

1. A method in which an oil based drilling fluid is used to carry debris out of a subsea bore hole and the debris is dumped in the sea while contaminated with the fluid and in which the oil of the oil base of the drilling fluid is a mineral oil that gives a mortality of brown shrimps of below 5% when tested in aerated sea water at 15°C for 24 hours at a concentration of 100 µl/l and that has a viscosity at 40°C of less than 6 cSt.
2. A method according to claim 1 in which the oil gives a mortality, when tested as in claim 1, of below 5% at 333 µl/l.
3. A method according to claim 1 in which the mineral oil has an aromatic content of less than 5%.
4. A method according to any preceding claim in which the mineral oil is a naphthenic oil.
5. A method according to any preceding claim in which the mineral oil is a paraffinic oil.
6. A method according to any preceding claim in which the oil has a viscosity at 20°C less than 10 cSt.
7. A method according to any preceding claim in which the oil has a viscosity at 40°C of from 1 to 5.5 cSt and at 20°C of from 1 to 8 cSt.



8. A method according to any preceding claim in which the oil has a viscosity at 20°C of from 1 to 7, at 40°C of from 1 to 5 and at 100°C of from 0.7 to 2.5 cSt.

9. A method according to any preceding claim in which the oil is less viscous than diesel oil.

10. A method according to any preceding claim in which the oil base consists of 30 to 100% by volume of the mineral oil and 70 to 0% water and the drilling fluid also includes drilling fluid additives selected from gelling agents, emulsifiers, bridging agents, weighting agents and lime.

11. A method according to any preceding claim substantially as herein described with reference to any of the examples.

12. An oil for use as the oil in an oil based drilling fluid and which is a mineral oil as defined in any of claims 1 to 9.

13. An oil for use as the oil in an oil based drilling fluid for carrying out of a subsea bore hole debris that is then dumped in the sea, and in which the oil is a mineral oil as defined in any of claims 1 to 9.

14. An oil according to claim 12 or claim 13 substantially as herein described with reference to any of the examples.

15. An oil based drilling fluid in which the oil of the oil base is a mineral oil as defined in any of claims 1 to 9.

16. An oil based drilling fluid for carrying out of a subsea bore hole debris that is then dumped in the sea and in which the oil of the oil base is a mineral oil as defined in any of claims 1 to 9.

17. A drilling fluid according to claim 15 or claim 16 substantially as herein described with reference to any of the examples.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 83/00049

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ³ : C 09 K 7/06; E 21 B 21/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC ³	C 09 K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y,P	FR, A, 2507616 (D. LARSON) 17 December 1982 see page 1, lines 1-22; page 2, lines 10-30; page 4, lines 31-35; page 5, lines 1-9	1,10,12,13,15,16
Y	FR, A, 2407252 (N.L. INDUSTRIES) 25 May 1979 see page 1, lines 1-32; page 2, lines 9-28; page 5, lines 22-30; page 8, lines 12,13; page 10, lines 23-25; example 4	1,4,10,12
T,P	Oil & Gas Journal, vol. 80, no. 25, June 1982 (Tulsa, Oklahoma, US) M. Jones et al.: "Drilling fluids bioassays and the OCS", pages 241-244, see the entire document and references	1,2
Y	US, A, 2698833 (D.L. WILSON) 4 January 1955 see column 3, examples 3-7; column 4, example 8; lines 78-82; claims 1-12 (cited in the application)	1,3,4,5,10,12 ./.
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